(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 773 298 B1

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
26.01.2000 Bulletin 2000/04

(51) Int Cl.[7]: **C12Q 1/06**, C23F 11/14, G01N 33/18

(21) Application number: **96308002.3**

(22) Date of filing: **05.11.1996**

(54) **Monitoring the level of microbiological activity of a fluid system**

Überwachung der mikrobiologischen Aktivität in einem Flüssigkeitssystem

Surveillance de taux d'activité dans un système de fluide

(84) Designated Contracting States:
DE ES FI FR GB IT SE

(30) Priority: **09.11.1995 US 556160**

(43) Date of publication of application:
14.05.1997 Bulletin 1997/20

(73) Proprietor: **NALCO CHEMICAL COMPANY**
Naperville Illinois 60563-1198 (US)

(72) Inventors:
- **Rao, Narasimha M.**
  Naperville, Illinois 60563 (US)
- **Hoots, John E.**
  St. Charles, Illinois 60174 (US)
- **Nghiem, Nhuan P.**
  Laguna Niguel, California 92677 (US)
- **Young, Paul R.**
  Wheaton, Illinois 60187 (US)

(74) Representative:
Harrison, David Christopher et al
MEWBURN ELLIS
York House
23 Kingsway
London WC2B 6HP (GB)

(56) References cited:
EP-A- 0 504 520
EP-A- 0 600 411
EP-A- 0 675 358
EP-A- 0 680 694
WO-A-95/33069
US-A- 4 108 790
US-A- 5 503 775

Printed by Jouve, 75001 PARIS (FR)

EP 0 773 298 B1 CORRIGENDUM issued on 26.04.2000 (bibliography updates included) - See p. 17 - 20

Description

[0001] The present invention is in the technical field of microbioreactive compositions and methods for monitoring and controlling the level of microbioactivity in fluid systems.

[0002] Microbiocides are added to aqueous systems in a variety of industrial and recreational applications. Some of these applications include the addition of microbiocides to control the growth of algae, bacteria, fungi and protozoa in industrial cooling water systems, recreational water systems such as pools and spas, the addition of microbiocides to control bacteria in the manufacture of paper, the use of microbiocides to control bacterial growth during the processing of raw sugar, and the like. Using various methods, the amount of a microbiocide in a system is monitored and controlled, balancing economic and environmental impacts against the effectiveness of the biocide. While particularly applicable to aqueous systems, the invention may also find utility in nonaqueous systems. As used herein, the terms "microbiocide" and "biocide" are used interchangeably and are meant to include chemicals used to control.

[0003] Current methods for the direct determination of the amounts of biological activity and the need for the addition of microbiocide in a fluid system tend to be time consuming measurements of the amount of bacterial growth in the system or wet-chemical analysis of samples for active microbiocide. These methods include culturing a sample taken from the fluid in the system to determine bacterial growth. If excessive bacterial growth is present, more microbiocide is generally fed into the system until a culture shows a steady or decreasing amount of microbiological growth. However, this method requires a culturing time of at least a day. Therefore, the ability to respond to microbiological problems in real time is not available with this method. Wet chemical analysis methods are time consuming, labor intensive and maybe subject to significant error when conducted in the field rather than a well equipped laboratory and do not give any information as to the level of microbiological control in the system.

[0004] EP-A-0 680 694 is directed to microbiocide compositions or systems containing microbiocide having added thereto a small quantity of inert fluorescent tracer material in an amount proportional to the quantity of microbiocide so that the amount of microbiocide added to the system can be measured and controlled on a continuous real-time basis by determining the level of fluorescence of the tracer added to the microbiocide. While this application teaches measurement of biological activity through system consumption, it does not teach or suggest the measurement of the biological activity in a fluid system by the direct reaction of the tracer with bacteria in the system. The term consumption, as used herein, does not include consumption of the bioreactive reagent due to excessive halogenation or corrosion within the fluid system.

[0005] The present invention is directed to compositions and methods using bioreactive reagents for on-line real-time determination of microbiological activity in an industrial system. The amount of bioreactive reagent added to the system and therefore, its expected concentration should no biodegradation occur in the system, is determined precisely. The actual concentration of the bioreactive reagent in the system is measured on-line. The extent of biological activity in the system is calculated as the difference between the two measurements. Based on the level of biological activity that is detected, the dosage of a microbiocide necessary to control the biological activity can be determined and controlled.

[0006] The use of inert tracer materials to monitor and control the concentration of treatment chemical products (e. g., those containing corrosion and scale inhibitors) in industrial water systems is well-known. Hoots (US-A-4,783,314) discloses the use of inert tracer materials for monitoring and controlling the concentration of treatment chemical products, corrosion and scale inhibitors, using fluorometry. Hoots et al. US-A-4,966,711 and 5,041,386) teaches the use of inert fluorescent additives which are added in direct proportion to the amount of a corrosion and/or scale inhibitor to monitor the concentration of a corrosion and/or scale inhibitor in a given industrial water system. US-A-4,992,380, 5,006,311 and 5,132,096 disclose methods and equipment to monitor fluorescent tracers used in industrial water treatment applications.

[0007] JP-B-55003668 (1980) discloses an atomic adsorption spectroscopy method for monitoring biocide concentrations by adding and measuring lithium salt materials to indirectly determine the concentration of microbiocides added to the system. This method requires the separate addition of tracer material and requires the use of atomic adsorption spectroscopy to obtain results. Atomic adsorption spectroscopy is expensive compared to fluorometry and has the disadvantage that atomic adsorption spectroscopy is not readily adaptable to field use for continuous monitoring and/or control of treatment dosage due to the complex equipment involved, as well as open flame and flammable gas supplies. In addition, this patent does not teach nor does it suggest the measurement of the biological activity or the level of the active biocide in a fluid system.

[0008] US-A-4,242,602 discloses an ultraviolet spectroscopy technique to monitor multiple water treatment components. The method involves the use of expensive analytical equipment along with computer hardware having specially written software. In addition, equipment must be calibrated on a site specific basis over a period of weeks or months and recalibration may be necessary if conditions in the water change. EP-A-466303 discloses a method involving the addition of a substance to treated water and how it reacts with the microbiocide, not the microbiological agents within the system. The substance reacting with the microbiocide is continuously measured and the concentration of the micro-

biocide is determined by loss of the substance. The method is cumbersome, requires special equipment, and two separate chemical feeds. The method is used to calculate the level of biocide in a system at a given time, but it does not measure the microbiological activity in the system.

[0009] Ideally, a bioreactive reagent composition and method would exist by which the level of microbiological activity in a system could be easily monitored, and in certain situations, by which an industrial microbiocide could be fed to the system in response to decreasing concentration or increasing consumption of the bioreactive reagent. The present invention solves many of the problems detailed above by providing an easy to use, continuous method for the determination and control of microbiological activity in fluid systems, particularly industrial water systems.

[0010] The invention is a method for monitoring the level of microbiological activity of a fluid system according to claim 1, and a composition for such a method according to claim 18.

[0011] The method comprises adding to the system, preferably an aqueous system, a formulation consisting of two components, namely, a bioreactive reagent and an inert compound. The inert compound is preferably fluorescent. They are added, perhaps in admixture, at a level to provide a system having concentrations at or greater than the minimum detection concentrations for the bioreactive reagent and the inert fluorescent compound in the system. The amount of the fluorescent bioreactive reagent added to the system is determined accurately by measuring the concentration of the inert compound in the system. The actual concentration of the fluorescent bioreactive reagent in the system is also measured on-line continuously. The difference between the expected and measured concentration (i. e., consumption) of the bioreactive reagent is a measure of the microbiological activity at a desired level. A microbiocide may than be added to the system to control the microbiological activity at a desired level.

[0012] In the drawings:

[0013] FIG. 1 graphically represents the biodegradation of the 5-methylbenzotriazole isomer after tolyltriazole spike.

[0014] FIG. 2 graphically represents the results from a Pilot Cooling Tower test showing the effect of bioreactive reagent consumption on microbiological population.

[0015] FIG. 3 graphically represents bacterial populations as a function of dosage of the 5-methylbenzotriazole isomer, the 4-methylbenzotriazole isomer and distilled water.

[0016] FIG. 4 graphically represents the data obtained from a respirometry experiment demonstrating the aerobic biodegradation of the 5-methylbenzotriazole isomer.

[0017] The present invention provides a method of monitoring and controlling microbiological activity in fluid systems. Although the invention is not limited to any particular source of water, preferably, cooling water systems, such as cooling towers, once-through cooling systems, cooling lake or pond systems, and spray ponds, are treated by the method and compositions of the invention. These cooling water systems are described in detail in the Nalco Water Handbook, 2nd ed., Ch. 34 (1988).

(Step a) Adding to the system a known amount of at least one bioreactive reagent of from about 10 ppb to about 100 ppm. The bioreactive reagent is added at a level to provide a system having a concentration of the bioreactive reagent at or greater than minimum detection concentration for such a bioreactive reagent in the system.

(Step b) The concentration of the bioreactive reagent is continuously measured by any known means.

(Step c) The concentration of bioreactive reagent present as measured in (Step b) is subtracted from the concentration of bioreactive reagent added in (Step a). The difference is used to calculate the level of consumption of the bioreactive reagent.

(Step d) The level of microbiological activity in the fluid system is calculated using the level of consumption of the bioreactive reagent.

[0018] A bioreactive reagent feed pump may be activated in response to concentration losses of bioreactive reagent below a pre-determined level and deactivated in response to concentrations of bioreactive reagent at or above the pre-determined level as determined by blowdown measurements, mass flow measurements of water loss, or any other known means used in measuring hydraulic losses in the fluid system. The concentration of the bioreactive reagent in the system can be measured by fluorescence. The concentration of the bioreactive reagent may be measured on an intermittent basis. The bioreactive reagent may be delivered to the system as a neat product or mixed with other treatment additives.

[0019] In addition to the dynamic operating conditions of a cooling water system, other significant variables and unknown factors are commonly encountered. For example, blowdown water (B) can be removed from the cooling system through a variety of ways (see equation 1), which unfortunately tend to be variable and ill-defined in nature. The rate at which water is specifically pumped from the cooling water system is defined as "recirculating water blowdown" (B_R), and even that rate is not always accurately known due to practical difficulties in measuring large volumes of water. In addition, ill-defined amounts of recirculating water (un-accounted system losses) are commonly removed from the cooling water system to be used in other areas of the industrial plant, defined as "plant blowdown" (B_p). Leakage of recirculating water (BL) and drift of liquid droplets from cooling tower (B_D) also add to unaccounted system

losses. A similar situation can occur with the makeup water, where the total makeup water rate (M) is the combined rate at which makeup water is specifically pumped into the recirculating system (M_R) and liquid originating from other sources (M'), (see equation 2). The complexity of the situation can be appreciated by considering equations 1 and 2.

$$B = B_R + B_P + B_L + B_D \quad \text{(eq 1)}$$

$$M = M_R + M' \quad \text{(eq 2)}$$

[0020] The feed rate of chemical treatment into the cooling water system is commonly based on estimated values for M_R or B_R, which means there can be considerable uncertainty regarding the concentration of the chemical treatment. When operating conditions of the cooling water system change, the feed rate of the chemical treatment should be adjusted. Those adjustments may or may not be made, depending on how carefully the cooling water system is monitored and controlled. Even when feed rates are adjusted, the concentration of chemical treatment within a cooling water system generally may respond slowly to the change (see equation 3).

$$t = (V_T/B) \ln (2) \quad \text{(eq 3)}$$

where t = response time for 50% of concentration increase to occur.

[0021] The inventive method for monitoring and controlling the microbiological activity of a fluid system comprises the following steps.

(Step a) Adding to the system a known amount of a bioreactive reagent of from about 10 ppb to about 100 ppm. The bioreactive reagent is 5-methylbenzotriazole, benzotriazole-5-carboxylic acid or butylbenzotriazole and is added at a level to provide a system having a concentration of the bioreactive reagent at or greater than minimum detection concentration for such a bioreactive reagent in the system.

(Step b) Adding a substantially inert compound in a known ratio of bioreactive reagent to the inert compound. The ratio of bioreactive reagent to inert compound can range from about 100:1 to about 1:100. The substantially inert compound is a mono -di- or - trisulfonated napthalene, a methyl naphthalene sulfonate or salt of any of these or a naphthalene sulfonate-formaldehyde polymer, a sulfonated derivative of pyrene or salt thereof added at a level to provide a system having the concentration of the inert compound at or greater than minimum detection concentrations for such a inert compound in the system.

(Step c) The concentration of the inert compound in the system is maintained at a constant predetermined level by adding inert compound and the bioreactive reagent in the initial ratio as required.

(Step d) The concentration of the inert compound is progressively measured by any known means.

(Step e) The concentration of the bioreactive reagent is progressively measured by any known means.

(Step f) The concentration of bioreactive reagent present as measured in step e) is subtracted from the concentration of inert compound present as measured in step d). The difference is used to calculate the level of consumption of the bioreactive reagent. Where the concentration of the inert compound is maintained at a pre-determined level, the amount of consumption of the bioreactive reagent is a measure of the difference between the amount of the reagent added to the system and the amount of the reagent measured in the system.

(Step g) The level of microbiological activity in the fluid system is calculated using the level of consumption of the bioreactive reagent.

[0022] By the terms "substantially inert" and "inert", it is meant that the compound (tracer) is not appreciably or significantly affected by any other chemistry in the system, or by other system parameters such as metallurgical composition, heat changes or heat content. Such compounds are not degraded by or deposited within the fluid system. This is termed an inert compound, inert to the system equipment and all chemistry in the system, so that the inert compound moves through the system unscathed and not altered to any significant or meaningful extent. The inert compounds used herein subscribe to the practical analytical chemistry requirement of loss equal to or less than 10%.

[0023] Both an inert compound feed pump and a bioreactive reagent feed pump may be activated in response to concentrations of inert compound below the pre-determined level and deactivated in response to concentrations of inert compound at or above the pre-determined level. In addition, the inert compound and bioreactive reagent can be added concurrently or as a mixture, using one feed pump. The concentrations of the inert compound and bioreactive reagents may be measured continuously or on an intermittent basis. The concentrations of the inert compound and

the bioreactive reagent in the system may be measured by fluorescence. The bioreactive reagent and the inert compound can be added to the system as a mixture.

[0024] The fluid system to which the present invention may find applicability includes various aqueous systems, such as a cooling water system or a waste treatment system. In addition, the fluid system may be a mixed organic/aqueous fluid system or a non-aqueous fluid system.

[0025] The method may comprise a further step of adding to the system an effective amount of microbiocide necessary to control the microbiological activity calculated in (Step g).

[0026] The microbiocide used in the present invention may be an oxidizing biocide selected from the group consisting of chlorine, bromine, iodine, hypochlorous acid, hypobromous acid, hypoiodous acid, stabilized hypochlorous acid, stabilized hypobromous acid, stabilized hypoiodous acid, and salts thereof. Alternatively, the microbiocide may be a non-oxidizing biocide selected from the group consisting of glutaraldehyde, isothiazolone, dibromonitrilopropionamide, metronidazole, dodecylguanidine, triazine, tributyltinoxide, cocodiamine, quaternary ammonium salt, carbamates, and copper sulfate. A microbiocidal chemical feed pump may be activated in response to levels of bioreactive reagent consumption at or above a pre-determined level of consumption and deactivated in response to levels of bioreactive reagent consumption below a pre-determined level of consumption.

[0027] The data obtained from system consumption measurement is used to quantitatively determine real-time system consumption of the bioreactive reagent. This data can be used to determine the extent to which undesirable system consumption has been reduced or eliminated by the addition of a microbiocide to the system.

[0028] A bioreactive composition, used in the present invention and the concentration of which when added to a fluid system is capable of being measured by known means in such system, is comprised of a diluent, one or more of the said bioreactive reagents, and at least one of the said substantially inert compounds, wherein the bioreactive reagents and the substantially inert compound is present in a ratio of from about 100:1 to about 1:100. More preferably, the ratio of bioreactive reagent to substantially inert compound is from about 100:1 to about 2:1, and most preferably from about 20:1 to about 2:1. The diluent may be water.

[0029] The inert compound may be soluble or evenly dispersible in the diluent. The inert compound is selected from a group consisting of mono-, di-, and tri- sulfonated naphthalenes, including their water soluble salts, particularly the various naphthalene mono- and di- sulfonic acid isomers, which are preferred inert compounds for use in the present invention. The naphthalene mono- and di- sulfonic acid isomers are water-soluble, generally available commercially and are easily detectable and quantifiable by know fluorescence analysis techniques. Preferred naphthalene mono- and di- sulfonic acid isomers are the water-soluble salts of naphthalene sulfonic acid (NSA), such as 1-NSA and 2-NSA, and naphthalene disulfonic acid (NDSA or NDA), for instance 1,2-NDSA, 1,3-NDSA, 1,4-NDSA, 1,5-NDSA, 1,6-NDSA, 1,7-NDSA, 1,8-NDSA, 2,3-NDSA, 2,4-NDSA, and so forth. In addition, methyl naphthalene sulfonates and water-soluble salts thereof, and naphthalene sulfonate-formaldehyde polymers are also useful as inert compounds in the present invention. Many of these inert compounds (mono-, di-, and tri- sulfonated naphthalene and mixtures thereof) are generally compatible with the environments of most aqueous systems employing industrial microbiocides.

[0030] Another group of inert fluorescent compounds that are preferred for use in the process of the present invention are the various sulfonated derivatives of pyrene, such as 1,3,6,8 pyrenetetrasulfonic acid, and the various water-soluble salts of such sulfonated pyrene derivatives. The composition of the present invention contains at least one inert compound that is selected from a group consisting of monosulfonated naphthalenes and water-soluble salts thereof, disulfonated naphthalenes and water-soluble salts thereof, trisulfonated naphthalenes and water-soluble salts thereof, methyl naphthalene sulfonates and water-soluble salts thereof, naphthalene sulfonate-formaldehyde polymers, sulfonated derivatives of pyrene and water-soluble salts thereof, and mixtures thereof.

[0031] As a general rule, inert tracers should be:

1. Thermally stable and not decompose at the temperature within the given system;
2. Detectable on a continuous or semicontinuous basis and susceptible to concentration measurements that are accurate, repeatable, and capable of being performed on the system;
3. Substantially foreign to the chemical species that are normally present in the water;
4. Substantially impervious to any of its own potential specific losses from the water of the system;
5. Substantially impervious to interference from, or biasing by, the chemical species that are normally present in the water;
6. Compatible with all treatment agents employed in the system in which the inert tracer may be used, and thus in no way reduce the efficacy thereof;
7. Compatible with all mechanical components of the system, and be stable in any storage and transportation conditions encountered; and,
8. Reasonably nontoxic and environmentally safe.

[0032] The bioreactive reagent is selected from methylbenzotriazole, benzotriazole-5-carboxylic acid, and butylben-

zotriazole.

[0033] As stated above, a preferred embodiment of the invention is a method for controlling the feed of an aqueous biocide into an aqueous system.

[0034] According to one embodiment of the invention, a known amount of a bioreactive reagent composition is added to an industrial or commercial cooling system to monitor microbiological activity. The bioreactive reagent is preferably added in a dosage of from 0.01 to 100 parts per million (ppm). More preferably, the bioreactive reagent is added to the cooling water in a final concentration of from 0.01 to about 20 ppm. A most preferred bioreactive reagent final concentration is from 0.01 to about 5 ppm. In one embodiment of the invention, bioreactive reagent is added to the cooling water continuously at a controlled rate to target or maintain a concentration of from 0.01 to 100 ppm. The bioreactive reagent may also be added intermittently to achieve a concentration of bioreactive reagent in the water from 0.01 to about 100 ppm. The cooling water may also contain corrosion inhibitors, such as biocides, phosphates, benzotriazole, napthalenetriazole, molybdates, zinc, phosphonates, and polymer treatment programs. These corrosion inhibitors may be added with the bioreactive reagent or separately.

[0035] Several different methods by which the bioreactive reagent concentration can be measured are described below.

Fluorescence Emission Spectroscopy

[0036] The detection and quantification of specific substances by fluorescence emission spectroscopy is founded upon the proportionality between the amount of emitted light and the amount of a fluoresced substance present. When energy in the form of light, including ultra violet and visible light, is directed into a sample cell, fluorescent substances therein will absorb the energy and then emit that energy as light having a longer wavelength than the absorbed light. The amount of emitted light is determined by a photodetector. In practice, the light is directed into the sample cell through an optical light filter so that the light transmitted is of a known wavelength, which is referred to as the excitation wavelength and generally reported in nanometers ("nm"). The emitted light is similarly screened through a filter so that the amount of emitted light is measured at a known wavelength or a spectrum of wavelengths, which is referred to as the emission wavelength and generally also reported in nanometers. When the measurement of specific substances or categories of substances at low concentrations is desired or required, such as often is the case for the process of the present invention, the filters are set for a specific combination of excitation and emission wavelengths, selected for substantially optimum low-level measurements.

[0037] Fluorescence emission spectroscopy is one of the preferred analysis techniques for the process of the present invention. Some naturally fluorescent compounds are also water treatment agents, and thus may be among the normal components of cooling water, such as aromatic organic corrosion inhibitors, such as aromatic (thio)(tri)azoles.

[0038] In general for most fluorescence emission spectroscopy methods having a reasonable degree of practicality, it is preferable to perform the analysis without isolating in any manner the fluorescent tracer. Thus, there may be some degree of background fluorescence. In instances where the background fluorescence is low, the relative intensities (measured against a standard fluorescent compound at a standard concentration and assigned a relative intensity for instance 100) of the fluorescence of the tracer or compound of interest is very high versus the background, for instance a ratio of 100/10 or 500/10 when certain combinations of excitation and emission wavelengths are employed even at low fluorescent compound concentrations, and such ratios would be representative of relative performance (under like conditions) of respectively 10 and 50. For most cooling water backgrounds, a compound that has a relative performance (fluorescence of tracer or compound of interest versus background) of at least about 5 at a reasonable concentration is very suitable as a fluorescent tracer itself or as a tagging agent for water treatment polymers and the like when such compounds contain an appropriate reactive group for the tagging reaction. When there is or may be a specific chemical specie of reasonably high fluorescence in the background, the tracer and the excitation and/or emission wavelengths often can be selected to nullify or at least minimize any interference of the tracer measurements(s) caused by the presence of such specie.

[0039] Continuous on-stream monitoring of chemical tracers by fluorescence emission spectroscopy and other analysis methods is described in U. S. Patent No. 4,992,380, B. E. Moriarity, J. J. Hickey, W. H. Hoy, J. E. Hoots and D. A. Johnson, issued February 12, 1991, incorporated herein by reference.

Combined HPLC-Fluorescence Analysis

[0040] The combination of high-performance liquid chromatograph ("HPLC") and fluorescence analyses of fluorescent tracers is a powerful measurement tool with the present invention, particularly when very low levels of the fluorescent tracer are used or the background fluorescence encountered would otherwise interfere with the efficacy of the fluorescence analysis. The HPLC-fluorescence analysis method allows the tracer compound and/or bioreactive reagent to be separated from the fluid matrix and then the tracer concentration can be measured. The combination of HPLC-

fluorescence analysis is particularly effective for measuring minute levels of tracer compound and/or bioreactive reagent in highly contaminated fluids.

[0041] The HPLC method can also be effectively employed to separate a tracer compound and/or bioreactive reagent from a fluid matrix for the purposes of then employing a tracer-detection method other than fluorescence analysis, and such other tracer-detection methods include without limitation light absorbance, post-column derivatization, conductivity and the like.

Colorimetry And Spectrophotometry Analysis

[0042] Colorimetry or spectrophotometry may be employed to detect and/or quantify a chemical tracer. Colorimetry is a determination of a chemical specie from its ability to absorb ultraviolet or visible light. One colorimetric analysis technique is a visual comparison of a blank or standard solution (containing a known concentration of the tracer specie) with that of a sample of the fluid being monitored. Another colorimetric method is the spectrophotometric method wherein the ratio of the intensities of the incident and the transmitted beams of light are measured at a specified wavelength by means of a detector such as a photocell or photomultiplier tube. Using a colorimetric probe, a fiber optic (dual) probe, such as a Brinkman PC-80 probe (570 nm filter), a sample solution is admitted to a flowcell in which the probe is immersed. One fiber optic cable shines incident light through the sample liquid onto a mirror inside the cell and reflected light is transmitted back through the sample liquid into a fiber optic cable and then to the colorimetric analyzer unit, which contains a colorimeter, by the other cable. The colorimeter has a transducer that develops an electrical analog signal of the reflected light characteristic of the tracer concentration. The voltage emitted by the transducer activates a dial indicator and a continuous line recorder printout unit. A set point voltage monitor may be employed to constantly sense or monitor the voltage analog generated by the colorimeter, and upon detection of a tracer signal (discussed below), a responsive signal may be transmitted to a responsive treatment agent feed line to commence or alter the rate of feed. Such a colorimetric analysis technique and the equipment that may be employed therefor are described in U. S. Patent No. 4,992,380, B. E. Moriarity, J. J. Hickey, W. H. Hoy, J. E. Hoots and D. A. Johnson, issued February 12, 1991, incorporated hereinto by reference. Chemical tracers suitable for use in conjunction with a colorimetric technique include transition metals (discussed below) and substances which show light absorbance which is detectable from that of other species present in the system fluid or substances which react with color-forming reagents to produce light absorbance which is detectable from that of other species present in the system fluids.

Transition Metal Analysis

[0043] A transition metal compound (transition metal ions, oxy-anions, cations and associated complexes) can be quantitatively measured by one or more of known techniques. Preferred techniques include colorimetry and fluorescence analysis. Another technique is molecular absorption. Molecular absorption in the ultra violet and visible region depends on the electronic structure of the molecule. The energy absorbed elevates electrons from orbitals in a lower-energy state to orbitals in a higher-energy state. A given molecule can absorb only certain frequencies because only certain states are possible in any molecule and the energy difference between any ground and excited state must be equal to the energy added. At a frequency that is absorbed by a molecule, the intensity of the incident energy is greater than the intensity of the emergent energy, and is a measure of the absorbance. A sample of the fluid being monitored may be compared to a calibration curve (absorbance versus concentration) prepared from standard solutions containing known concentrations of the transition metal (or other suitable tracer specie) to detect and determine the concentration of the tracer. A molecular absorption technique for transition metal tracers is described in U. S. Patent No. 4,992,380, B. E. Moriarity, J. J. Hickey, W. H. Hoy, J. E. Hoots and D. A. Johnson, issued February 12, 1991, incorporated hereinto by reference.

[0044] Analytical techniques for detecting the presence and/or concentration of a chemical specie without isolation thereof are within an evolving technology, and the above survey of reasonable analytical techniques for use in the process of the present invention may presently not even be exhaustive, and most likely techniques equivalent to the above for the purposes of the present invention will be developed in the future.

[0045] A chemical specie may be selected for a given process based on a preference for one or more analytical techniques, or an analytical technique may be selected for a given process based on a preference for one or more chemical tracers. In preferred embodiments, the chemical compound(s) selected as the tracer should be soluble in at least one, and more preferably in both, of the temperature-conditioning fluid and process fluid of the industrial process, at least at the concentration level(s) expected in the respective fluid.

[0046] The compositions and methods of this invention are applicable to both so-called non-oxidizing and oxidizing microbiocides. Examples of commonly available oxidizing biocides to which this invention may find utility include but are not limited to the following: hypochlorite bleach, hydrogen peroxide, peracetic acid, potassium monopersulfate, bromochlorodimethylhydantoin, dichloromethylethylhydantoin, and chloroisocyanurate. The compositions and meth-

ods of this invention are also applicable to ingredients that later react to form biocidal compositions. Examples of materials of this type include the reaction of sodium bromide with chlorine to produce hypobromite bleach.

[0047] Examples of commonly available non-oxidizing biocides to which this invention may find applicability include but are not limited to the following:

dibromonitrilopropionamide, thiocyanomethylbenzothiazole, methyldithiocarbamate, tetrahydrodimethylthiodiazonethione, tributyltin oxide, bromonitropropanediol, bromonitrostyrene, methylene bisthiocyanate, chloromethyl/methylisothiazolone, bensiosthiazolone, dodecylguanidine hydrochloride, polyhexamethylene biguanide, tetrakishydroxymethyl phosphonium sulfate, glutaraldehyde, alkyldimethylbenzyl ammonium chloride, didecyldimethylammonium chloride, poly[oxyethylene(dimethyliminio) dichloride], decylthioethanamine, and terbuthylazine.

[0048] By utilizing compositions of this invention, along with appropriate fluorescent measuring devices, an accurate and continuous method for determining the levels of microbiological activity such as, but not limited to, industrial water treatment and papermaking is achieved.

[0049] Most importantly, the method allows the on-line measurement of microbiological activity in the system and makes it possible to respond to system changes and upsets in a timely fashion. Since biocide is fed based on measured microbiological activity, the invention also provides a means to minimize the dosage of biocide required to achieve microbiological control by eliminating excess feed. The invention also provides a means to control the treatment regime, e.g. the frequency and amplitude of microbiocide dosage in order to improve the antimicrobial performance of the treatment. One way that the tracer compositions of the subject invention- are monitored, however, not limited to, is much the same way as disclosed in U.S. Patent Nos. 4,992,380 and 4,783,314, both of which are hereinafter incorporated by reference into the specification.

[0050] The invention may also be employed to automatically add microbiocide into a system, thereby keeping the biocide at a level at or greater than its minimum inhibitory concentration or to automatically add tracer material into a system, thereby keeping the tracer at a level at or greater than its minimum detection concentration. In this embodiment of the invention, a formulation consisting of a mixture of a bioreactive reagent and an inert compound in a known ratio are added to the system. The concentration of the bioreactive reagent and inert reagent are continuously determined by fluorescence measurement. The concentration of the inert fluorescent compound is maintained at a constant value by feeding additional formulation as needed to compensate for water losses (blowdown, drift, et.) from the system. In the event the fluorescence level of the bioreactive reagent decreases from a present known value, the fluorometer sends a signal to a controller, or to a pump to feed additional biocide until the level of the bioreactive reagent (or consumption of bioreactive reagent) reached a predetermined set point. Means for allowing a fluorometer to send a signal to a pump, alarm device, or modem are generally known in the art, and will not be discussed herein. This method can be used to keep the biocide level in a system at or slightly above the specified minimum inhibitory concentration of the biocide in the system. In another embodiment of the invention, a formulation consisting of a mixture of a bioreactive reagent and an inert compound in a known ratio are added to the system. In the event the fluorescence level of the bioreactive reagent decreases from a present known value, the fluorometer sends a signal to a controller, or to a pump to feed additional formulation and/or biocide until the level of the bioreactive reagent reached a pre-set value. The difference between the inert fluorescent compound and the bioreactive reagent concentrations is a measure of the microbiological activity.

[0051] The compositions of this invention are- measured preferably by fluorometry. In this method, a sample of the system containing the tracer material is excited by passing a light wave of known wave length into the sample. The wavelength utilized is determined by the frequency at which the sample fluoresces, and if other constituents in the system also fluoresce at a known -wave length after excitation at this frequency. After excitation of the sample, the emission caused by the excitation is measured. Fluorometers for this purpose are commercially available from a variety of sources. Preferred fluorometers for this purpose are available from the Nalco Chemical Company, Naperville, Illinois under the trade name TRASAR®.

[0052] The following examples are presented to describe preferred embodiments and utilities of the invention and are not meant to limit the invention unless otherwise stated in the claims appended hereto.

Example 1

[0053] A field sample of discharge water from a utility treated with a mixed tolyltriazole preparation (TT), containing 40% of the 4-MeBT isomer and 60% of the 5-MeBT isomer, was analyzed for 4-MeBT and 5-MeBT using HPLC and found to contain only 4-MeBT. This sample was spiked with 2 ppm. of a mixed isomer tolyltriazole preparation (1.16 ppm 5-MeBT and 0.84 ppm 4-MeBT). The sample was periodically assayed for 4-MeBT and 5-MeBT. It was found that the 5-MeBT levels had not changed in about 10 hours. When measured at the end of 40 hours, the 5-MeBT had disappeared completely (Figure 1). This type of degradation, following an initial acclimation period is very typical of microbial degradation. Sulfuric acid was added to the sample in order to lyse any bacteria. The sample was analyzed directly using fluorescence as well as HPLC. 5-MeBT was not observed in either assay.

Example 2

[0054] A field sample of discharge water from a utility was analyzed for TT by HLPC and found to contain only 4-MeBT. The sample was split into 8 fractions. One fraction was left as is and spiked with 2 ppm TT as in Example 1. The other seven fractions were subjected to one of the following processes and then spiked with 2 ppm TT:

Sample #	Treatment
1	None
The following samples were treated to eliminate microbiol agents from the water sample:	
2	Filtration through 0.2μ filter
3	Treatment with 200 ppm glutaraldehyde
4	Ozonation for 5 minutes
5	Autoclaving for 15 minutes
6	Acidification to reduce pH < 1 with H_2SO_4
7	Addition of CH_3CN to get final concentration of 20%

[0055] Additionally, sample 8 was spiked with 2 ppm TT and chilled in a refrigerator. It was found that in sample 1 with no treatment, 5-MeBT disappeared in approximately 2 days. In samples 2 through 8, 5-MeBT was stable for up to one month, analysis was not performed after this time. Since all the treatments listed in samples nos. 2 through 8 either were treated with a bactericide or a treatment in inhibit bacterial metabolism, preservation of the 5-MeBT in these samples demonstrates a microbiological mode of degradation. When sample no. 8, the chilled sample, was kept at room temperature, the 5-MeBT disappeared in about 2 days. This provides evidence of a microbiological degradation mechanism for 5-MeBT.

Example 3

[0056] A Pilot Cooling test (PCT) was conducted using a mixed isomer tolyltriazole product at a 75 ppm maintenance TT dosage level. The product was fed continuously in order to maintain the level. Samples were collected daily and TT levels were analyzed using HPLC. No chlorination was used for the first 13 days. During this period, the 5-MeBT to 4-MeBT ratio stayed constant at approximately 1.5 to 1 for the first 8 days and began to drop thereafter. The drop in the 5-MeBT to 4-MeBT ratio coincided with a precipitous rise in the microbiological counts. The ratio dropped to 0.29 to 1 on the 13th day of the test, at which time the basin was slugged with bleach to achieve a 0.1 ppm residual and then fed bleach continually to maintain 0.1 - 0.2 ppm residuals. The 5-MeBT to 4-MeBT ratio began to climb back up, reaching 1.5 to 1 in approximately 3 days. The total microbiological counts, in the mean time dropped to <100 CFU/ml. On the 19th day of the test, the chlorine feed was shut off again. The 5-MeBT to 4-MeBT ratio started to decrease again, reaching approximately 0.27 to 1 in about 9 days and staying constant thereafter. The decrease in 5-MeBT to 4-MeBT ratio once again coincided with the increase in microbiological counts. Results are summarized in Figure 2. This example simulates the degradation of 5-MeBT due to microbiological activity in a cooling tower.

Example 4

[0057] A field water sample from the PCT test in Examples 1 and 2 was split into three portions. To the first portion, 5-MeBT was repeatedly spiked after the previous spike disappeared to achieve a total concentration of 1150 ppm. To the second portion, 1150 ppm of 4-MeBT was added in an analogous manner. The third portion was spiked with distilled water. Samples were withdrawn at various intervals and assayed for total aerobic counts. The results are shown in Figure 3. It can be clearly seen that the degradation of the 5-MeBT isomer results in a significant increase in total cell counts. No such increase was found for the 4-MeBT isomer and control sample.

[0058] At the end of the experiment, the samples were filtered through a 0.2μ filter and submitted for Dissolved Organic Carbon (DOC) analysis. It was found that the DOC of the sample with 5-MeBT addition had increased by 60 ppm over the control. If no degradation or assimilation into cell mass occurred, the DOC should have increased by 726 ppm over the control sample. In contrast, the DOC of the sample with 4-MeBT addition increased by 770 ppm over the control sample. Addition of 15% sulfuric acid to the 5-MeBT spiked solutions to lyse the cells does not increase the 5-MeBT concentration, ruling out adsorption effects. This example illustrates that most of the organic carbon was assimilated into cell mass or degraded substantially.

Example 5

[0059] Three liters of a solution containing 1 ml/L of heavy metals, 1 g/L of NH_4Cl, 0.5 g/L of K_2HPO_4 and 0.1 g/L of $MgSO_4$ was prepared. The pH was adjusted to 7 with H_3PO_4. The solution was then split into three parts. To the first part, 50 ppm of 5-MeBT was spiked. To the second part, 50 ppm of 4-MeBT was spiked. To the third part, distilled water was spiked. To each of the parts, 10 ml of an inoculum containing bacteria acclimated with 5-MeBT (from 5-MeBT spiked sample in Examples 1 and 2) was added. The three solutions were then transferred to respirometry bottles and the oxygen consumption by the bacteria in the bottles was measured as a function of time. It was found that the 5-MeBT spiked samples showed a significantly higher oxygen consumption (55 mg per 50 mg of 5-MeBT), than the 4-MeBT and distilled water spiked samples. The 5-MeBT spiked sample was additionally spiked with 100, 150 and 200 ppm of 5-MeBT, each time waiting for the oxygen consumption from the previous spike to level off. The results are shown in Figure 4. This example illustrates an aerobic oxidation mechanism for the microbial degradation of the 5-MeBT isomer, however, the invention is not limited to aerobic mechanisms only.

Example 6

[0060] Additional respirometry experiments were carried out as described in Example 8. To the first part, distilled water was spiked. To the second part, 25 ppm of 5-MeBT was spiked. To the third part, 165 ppm of benzotriazole-5-carboxylic (BZT-5-C) was spiked. To each of the parts, 300 of an inoculum containing bacteria acclimated with 5-MeBT was added. The three solutions were then transferred to respirometry bottles and the oxygen consumption by the bacteria in the bottles was measured as a function of time. It was found that the 5-MeBT and BZT-5-C spiked samples showed significantly higher oxygen consumptions than the distilled water spiked sample. The 5-MeBT spiked sample was additionally spiked with 50, 120 and 240 ppm of 5-MeBT, each time waiting for the oxygen consumption from the previous spike to level off. The BZT-5-C spike sample was additionally spiked with 165, 165 and 250 ppm of BZT-5-C, each time waiting for the oxygen consumption from the previous spike to level off. Samples were drawn before each spike and assayed for the spiked compound by HPLC, for DOC and for total viable aerobic counts. The results showed that each spike of 5-MeBT-and BZT-5-C was accompanied by a proportional amount of oxygen uptake. It was seen that approximately 95% of the spiked DOC disappeared. In addition of 5-MeBT and BZT-5-C resulted in an increase of approximately three orders of magnitude in the total viable aerobic counts. This example illustrates an aerobic oxidation mechanism for the microbial degradation of both 5-MeBT and BZT-5-C.

[0061] Changes can be made in the composition, operation and arrangement of the method of the present invention described herein without departing from the concept and scope of the invention as defined in the following claims:

Claims

1. A method for monitoring and controlling the microbiological activity of a fluid system which comprises:

   a. adding to the system a known amount of a bioreactive reagent, chosen from 5-methylbenzotriazole, benzotriazole-5-carboxylic acid and butylbenzotriazole, said bioreactive reagent being added at a level of from about 10 ppb to about 100 ppm, said level being sufficient to provide a system having a concentration of said bioreactive reagent at or greater than the minimum detection concentration for such bioreactive reagent in the system;

   b. adding a substantially inert compound, chosen from:

      i) monosulfonated naphthalenes and water-soluble salts thereof;
      ii) disulfonated naphthalenes and water-soluble salts thereof;
      iii) trisulfonated naphthalenes and water-soluble salts thereof;
      iv) methyl naphthalene sulfonates and water-soluble salts thereof;
      v) naphthalene sulfonate-formaldehyde polymers;
      vi) sulfonated derivatives of pyrene and water-soluble salts thereof; and
      vii) mixtures thereof;

      with said substantially inert compound being added in a known ratio of said bioreactive reagent to said inert compound, said substantially inert compound being added at a level to provide a system having the concentration of said inert compound at or greater than minimum detection concentrations for such inert compound in the system;

   c. maintaining the concentration of said inert compound in the system at a constant predetermined level by

adding inert compound and said bioreactive reagent in the initial ratio as required;
d. progressively measuring the concentration of said inert compound by a known means;
e. progressively measuring the concentration of said bioreactive reagent by a known means;
f. subtracting the concentration of bioreactive reagent present as measured in step e) from the concentration of inert compound present as measured in step d) and calculating the level of consumption of said bioreactive reagent; and
g. calculating the level of microbiological activity in the fluid system.

2. A method according to claim 1, wherein a feed pump is activated to feed inert compound bioreactive reagent in response to concentrations of inert compound below the predetermined level and is deactivated in response to concentrations of inert compound at or above the predetermined level.

3. A method according to claim 1, wherein inert compound and bioreactive reagent feed pumps are activated in response to concentrations of inert compound below the predetermined level and are deactivated in response to concentrations of inert compound at or above the predetermined level.

4. A method according to any one of the preceding claim, wherein the bioreactive reagent and the inert compound are added to the system as a mixture.

5. A method according to any one of the preceding claims, wherein the concentration of the inert compound in the system is measured by fluorescence.

6. A method according to any one of the preceding claims, wherein the concentration of the inert compound and/or of the bioreactive reagent is measured intermittently.

7. A method according to any one of claims 1 to 5 wherein the measurement in step e is continuous.

8. A method according to any one of the preceding claims, wherein the fluid system is an aqueous system.

9. A method according to claim 8, wherein the fluid system is a cooling water system or a waste treatment system.

10. A method according to any one of claims 1 to 7, wherein the fluid system is a mixed organic/aqueous fluid system.

11. A method according to any one of claims 1 to 7, wherein the fluid system is a non-aqueous fluid system.

12. A method according to any one of the preceding claims, which further comprises a step of adding to the system an effective amount of microbiocide necessary to control the microbiological activity calculated in step g).

13. A method according to claim 12, wherein the microbiocide is an oxidizing biocide selected from the group consisting of chlorine, bromine, iodine, hypochlorous acid, hypobromous acid, hypoiodous acid, stabilized hypochlorous acid, stabilized hypobromous acid, stabilized hypoiodous acid, and salts thereof.

14. The method according to claim 13, wherein the microbiocide is a non-oxidizing biocide selected from the group consisting of glutaraldehyde, isothiazolone, dibromonitrilopropionamide, metronidazole, dodecylguanidine, triazine, tributyltinoxide, cocodiamine, quaternary ammonium salt, carbamates, and copper sulfate.

15. The method according to any one of claims 12, 13 or 14, wherein a microbiocidal chemical feed pump is activated in response to levels of bioreactive reagent consumption at or above a predetermined level of consumption and is deactivated in response to levels of bioreactive reagent consumption below a predetermined level of consumption.

16. The method according to claim 15, wherein the data from system consumption measurement is used to quantitatively determine real-time system consumption of the bioreactive reagent.

17. The method according to claim 12, wherein the data from the system consumption measurement is used to determine the extent to which undesirable system consumption has been reduced or eliminated by the addition of a microbiocide to the system.

18. A bioreactive composition, the concentration of which when added to a fluid system is capable of being measured by known means in such system, the composition comprising:

    a. diluent;
    b. one or more bioreactive reagents chosen from 5-methylbenzotriazole, benzotriazole-5-carboxylic acid, or butylbenzotriazole; and
    c. at least one substantially inert compound, soluble or evenly dispersible in the diluent and chosen from

        a. monosulfonated naphthalenes and water-soluble salts thereof;
        b. disulfonated naphthalenes and water-soluble salts thereof;
        c. trisulfonated naphthalenes and water-soluble salts thereof;
        d. methyl naphthalene sulfonates and water-soluble salts thereof;
        e. naphthalene sulfonate-formaldehyde polymers;
        f. sulfonated derivatives of pyrene and water-soluble salts thereof; and
        g. mixtures thereof

    wherein the bioreactive reagent(s) and the substantially inert compound(s) are present at a ratio of from about 100:1 to about 1:100.

Patentansprüche

1. Verfahren zur Überwachung und Bekämpfung der mikrobiologischen Aktivität in einem Flüssigkeitssystem, welches umfaßt:

    a) die Zugabe einer bekannten Menge eines bioreaktiven Reagens zum System, wobei das Reagens aus 5-Methylbenzotriazol, Benzotriazol-5-carbonsäure und Butylbenzotriazol ausgewählt ist und in einer Menge von etwa 10 ppb bis etwa 100 ppm zugegeben wird, wobei die Menge ausreicht, um ein System mit einer Konzentration des bioreaktiven Reagens gleich oder über der Nachweisgrenzkonzentration für solche bioreaktive Reagenzien im System bereitzustellen;
    b) die Zugabe einer im wesentlichen inerten Verbindung, ausgewählt aus:

        i) monosulfonierten Naphthalinen und wasserlöslichen Salzen davon;
        ii) disulfonierten Naphthalinen und wasserlöslichen Salzen davon;
        iii) trisulfonierten Naphthalinen und wasserlöslichen Salzen davon;
        iv) Methylnaphthalinsulfonaten und wasserlöslichen Salzen davon;
        v) Naphthalinsulfonat-Formaldehyd-Polymeren;
        vi) sulfonierten Pyrenderivaten und wasserlöslichen Salzen davon;
        vii) Gemischen davon;

    wobei die im wesentlichen inerte Verbindung in einem bekannten Verhältnis von bioreaktivem Reagens zur inerten Verbindung zugegeben wird, wobei die im wesentlichen inerte Verbindung in einer Menge zugegeben wird, um ein System mit einer Konzentration der inerten Verbindung gleich oder über den Nachweisgrenzkonzentrationen für solche inerte Verbindungen im System bereitzustellen;

    c) das Halten der Konzentration der inerten Verbindung im System auf einem konstanten vorbestimmten Wert durch Zugabe von inerter Verbindung bzw. bioreaktivem Reagens, wie erforderlich, im anfänglichen Verhältnis;
    d) das schrittweise Messen der Konzentration der inerten Verbindung auf bekannte Weise;
    e) das schrittweise Messen der Konzentration des bioreaktiven Reagens auf bekannte Weise;
    f) das Subtrahieren der in Schritt e) gemessenen, herrschenden Konzentration an bioreaktivem Reagens von der in Schritt d) gemessenen, herrschenden Konzentration an inerter Verbindung und das Berechnen des Verbrauchs an bioreaktivem Reagens; sowie
    g) das Berechnen des Ausmaßes mikrobiologischer Aktivität im Flüssigkeitssystem.

2. Verfahren nach Anspruch 1, worin eine Förderpumpe eingeschaltet wird, um als Reaktion auf Konzentrationen der inerten Verbindung unter dem vorbestimmten Wert inerte Verbindung und bioreaktives Reagens zuzuführen, und als Reaktion auf Konzentrationen der inerten Verbindung auf oder über dem vorbestimmten Wert ausgeschaltet wird.

3. Verfahren nach Anspruch 1, worin Förderpumpen für inerte Verbindung und bioreaktives Reagens als Reaktion auf Konzentrationen der inerten Verbindung unter dem vorbestimmten Wert eingeschaltet werden und als Reaktion auf Konzentrationen der inerten Verbindung auf oder über dem vorbestimmten Wert ausgeschaltet werden.

4. Verfahren nach einem der vorangegangenen Ansprüche, worin das bioreaktive Reagens und die inerte Verbindung dem System als Gemisch zugegeben werden.

5. Verfahren nach einem der vorangegangenen Ansprüche, worin die Konzentration der inerten Verbindung im System mittels Fluoreszenz gemessen wird.

6. Verfahren nach einem der vorangegangenen Ansprüche, worin die Konzentration der inerten Verbindung und/oder des bioreaktiven Reagens intermittierend gemessen wird.

7. Verfahren nach einem der Ansprüche 1 bis 5, worin die Messung in Schritt e kontinuierlich erfolgt.

8. Verfahren nach einem der vorangegangenen Ansprüche, worin das Flüssigkeitssystem ein wäßriges System ist.

9. Verfahren nach Anspruch 8, worin das Flüssigkeitssystem ein Kühlwassersystem oder ein Abfallbehandlungssystem ist.

10. Verfahren nach einem der Ansprüche 1 bis 7, worin das Flüssigkeitssystem ein gemischtes organisches/wäßriges Flüssigkeitssystem ist.

11. Verfahren nach einem der Ansprüche 1 bis 7, worin das Flüssigkeitssystem ein nicht-wäßriges Flüssigkeitssystem ist.

12. Verfahren nach einem der vorangegangenen Ansprüche, welches weiters einen Schritt der Zugabe einer wirksamen Menge Mikrobiozid, die notwendig ist, um die in Schritt g) berechnete mikrobiologische Aktivität zu bekämpfen, zum System umfaßt.

13. Verfahren nach Anspruch 12, worin das Mikrobiozid ein oxidierendes Biozid ist, das aus der aus Chlor, Brom, Iod, hypochloriger Säure, hypobromiger Säure, hypoiodiger Säure, stabilisierter hypochloriger Säure, stabilisierter hypobromiger Säure, stabilisierter hypoiodiger Säure und Salzen davon bestehenden Gruppe ausgewählt ist.

14. Verfahren nach Anspruch 13, worin das Mikrobiozid ein nicht-oxidierendes Biozid ist, das aus der aus Glutaraldehyd, Isothiazolon, Dibromnitrilopropionamid, Metronidazol, Dodecylguanidin, Triazin, Tributylzinnoxid, Kokosdiamin, quaternären Ammoniumsalzen, Carbamaten und Kupfersulfat bestehenden Gruppe ausgewählt ist.

15. Verfahren nach einem der Ansprüche 12, 13 oder 14, worin eine Förderpumpe für Mikrobiozidchemikalie als Reaktion auf Verbrauchsmengen an bioreaktivem Reagens auf oder über einem vorbestimmten Wert eingeschaltet und als Reaktion auf Verbrauchsmengen an bioreaktivem Reagens unter einem vorbestimmten Wert ausgeschaltet wird.

16. Verfahren nach Anspruch 15, worin die Daten der Systemverbrauchsmessung verwendet werden, um den Echtzeit-Systemverbrauch an bioreaktivem Reagens quantitativ zu bestimmen.

17. Verfahren nach Anspruch 12, worin die Daten der Systemverbrauchsmessung verwendet werden, um das Ausmaß zu bestimmen, in dem unerwünschter Systemverbrauch durch Zugabe eines Mikrobiozids zum System verringert oder beseitigt wurde.

18. Bioreaktive Zusammensetzung, deren Konzentration bei Zugabe zu einem Flüssigkeitssystem auf bekannte Weise in einem solchen System gemessen werden kann, wobei die Zusammensetzung umfaßt:

a) Verdünner;
b) ein oder mehrere bioreaktive Reagenzien, ausgewählt aus 5-Methylbenzotriazol, Benzotriazol-5-carbonsäure oder Butylbenzotriazol; und
c) zumindest eine im wesentlichen inerte Verbindung, die im Verdünner löslich oder gleichmäßig dispergierbar ist und ausgewählt ist aus:

a) monosulfonierten Naphthalinen und wasserlöslichen Salzen davon;
b) disulfonierten Naphthalinen und wasserlöslichen Salzen davon;
c) trisulfonierten Naphthalinen und wasserlöslichen Salzen davon;
d) Methylnaphthalinsulfonaten und wasserlöslichen Salzen davon;
e) Naphthalinsulfonat-Formaldehyd-Polymeren;
f) sulfonierten Pyrenderivaten und wasserlöslichen Salzen davon;
g) Gemischen davon;

worin das/die bioreaktive/n Reagens/Reagenzien und die im wesentlichen inerte(n) Verbindung(en) in einem Verhältnis von etwa 100:1 bis etwa 1:100 vorliegen.

Revendications

1. Méthode de surveillance et de contrôle de l'activité microbiologique dans un système de fluide qui comprend :

a. ajouter au système une quantité connue d'un réactif bioréactif, choisi parmi le 5-méthylbenzotriazole, l'acide benzotriazole-5-carboxylique et le butylbenzotriazole, ledit réactif bioréactif étant ajouté à un niveau d'environ 10 ppb à environ 100 ppm, ledit niveau étant suffisant pour donner un système ayant une concentration dudit réactif bioréactif à ou plus grande que la concentration minimale de détection pour ledit réactif bioréactif dans le système ;
b. ajouter un composé sensiblement inerte, choisi parmi :

i) des naphtalènes monosulfonés et leurs sels solubles dans l'eau ;
ii) des naphtalènes disulfonés et leurs sels solubles dans l'eau ;
iii) des naphtalènes trisulfonés et leurs sels solubles dans l'eau ;
iv) des méthyl naphtalènes sulfonates et leurs sels solubles dans l'eau ;
v) des polymères de sulfonate de naphthalèneformaldéhyde ;
vi) des dérivés sulfonés de pyrène et leurs sels solubles dans l'eau ;et
vii) leurs mélanges ;
ledit composé sensiblement inerte étant ajouté à un rapport connu dudit réactif bioréactif audit composé inerte, ledit composé sensiblement inerte étant ajouté à un niveau pour donner un système ayant la concentration dudit composé inerte à ou plus grande que les concentrations minimales de détection pour un tel composé inerte dans le système ;

c. maintenir la concentration dudit composé inerte dans le système à un niveau prédéterminé constant en ajoutant ledit composé inerte et ledit réactif bioréactif au rapport initiale requis ;
d. mesurer progressivement la concentration dudit composé inerte par un moyen connu ;
e. mesurer progressivement la concentration dudit réactif bioréactif par un moyen connu ;
f. soustraire la concentration du réactif bioréactif présent, telle que mesurée à l'étape e) de la concentration du composé inerte présent mesurée à l'étape d) et calculer le niveau de consommation dudit réactif bioréactif ; et
g. calculer le niveau d'activité microbiologique dans le système de fluide.

2. Méthode selon la revendication 1, où une pompe d'alimentation est activée pour fournir le composé inerte réactif bioréactif en réponse à des concentrations du composé inerte en dessous du niveau prédéterminé et est désactivée en réponse à des concentrations du composé inerte à ou au-dessus du niveau prédéterminé.

3. Méthode selon la revendication 1 où les pompes d'alimentation du composé inerte et du réactif bioréactif sont activées en réponse à des concentrations du composé inerte en dessous du niveau prédéterminé et sont désactivées en réponse à des concentrations du composé inerte à ou au-dessus du niveau prédéterminé.

4. méthode selon l'une quelconque des revendications précédentes, où le réactif bioréactif et le composé inerte sont ajoutés au système en un mélange.

5. Méthode selon l'une quelconque des revendications précédentes, où la concentration du composé inerte dans le système est mesurée par fluorescence.

6. Méthode selon l'une quelconque des revendications précédentes, où la concentration du composé inerte et/ou du réactif bioréactif est mesurée par intermittence.

7. Méthode selon l'une quelconque des revendications 1 à 5, où la mesure à l'étape e) est continue.

8. Méthode selon l'une quelconque des revendications précédentes, où le système de fluide est un système aqueux.

9. Méthode selon la revendication 8, où le système de fluide est un système d'eau de refroidissement ou un système de traitement de résidus.

10. Méthode selon l'une quelconque des revendications 1 à 7, où le système de fluide est un système de fluide organique/aqueux mélangé.

11. Méthode selon l'une quelconque des revendications 1 à 7, où le système de fluide est un système de fluide non aqueux.

12. Méthode selon l'une quelconque des revendications précédentes, qui comprend de plus une étape d'addition, au système, d'une quantité efficace d'un microbiocide, nécessaire pour contrôler l'activité microbiologique calculée à l'étape g).

13. Méthode selon la revendication 12, où le microbiocide est un biocide oxydant sélectionné dans le groupe consistant en chlore, brome, iode, acide hypochloreux, acide hypobromeux, acide hypoiodeux, acide hypochloreux stabilisé, acide hypobromeux stabilisé, acide hypoiodeux stabilisé et leurs sels.

14. Méthode selon la revendication 13, où le microbiocide est un biocide non oxydant sélectionné dans le groupe consistant en glutaraldéhyde, isothiazolone, dibromonitrilopropionamide, métronidazole, dodécylguanidine, triazine, oxyde de tributylétain, cocodiamine, sel d'ammonium quarternaire, carbamates et sulfate de cuivre.

15. Méthode selon l'une quelconque des revendications 12, 13 ou 14, où une pompe d'alimentation du produit chimique biocide est activée en réponse à des niveaux de consommation du réactif bioréactif à ou au-dessus d'un niveau prédéterminé de consommation et est désactivée en réponse à des niveaux de consommation du réactif bioréactif en dessous d'un niveau prédéterminé de consommation.

16. Méthode selon la revendication 15, où les données d'une mesure de consommation du système sont utilisées pour déterminer quantitativement la consommation du réactif bioréactif, en temps réel, par le système.

17. Méthode selon la revendication 12, où les données de la mesure de la consommation du système sont utilisées pour déterminée l'étendue à laquelle une consommation non souhaitable du système a été réduite ou éliminée par l'addition d'un microbiocide au système.

18. Composition bioréactive, dont la concentration, lors de l'addition à un système de fluide, est capable d'être mesurée par un moyen connu dans un tel système, la composition comprenant :

    a. un diluant ;
    b. un ou plusieurs réactifs bioréactifs choisis parmi le 5-méthylbenzotrizole, l'acide benzotriazole-5-carboxylique ou le butylbenzotriazole;
    c. au moins un composé sensiblement inerte, soluble ou régulièrement dispersible dans le diluant et choisi parmi

        a. des naphtalènes monosulfonés et leurs sels solubles dans l'eau ;
        b. des naphtalènes disulfonés et leurs sels solubles dans l'eau ;
        c. des naphtalènes trisulfonés et leurs sels solubles dans l'eau ;
        d. des méthyl naphtalènes sulfonates et leurs sels solubles dans l'eau ;
        e. des polymères de naphtalène sulfonateformaldéhyde ;
        f. des dérivés sulfonés de pyrène et leurs sels solubles dans l'eau ; et
        g. leurs mélanges.

où le(s) réactif(s) bioréactif(s) et le(s) composé(s) sensiblement inerte(s) sont présents à un rapport d'environ 100 :

1 à environ 1:100.

[drawing(s) replaced or added]

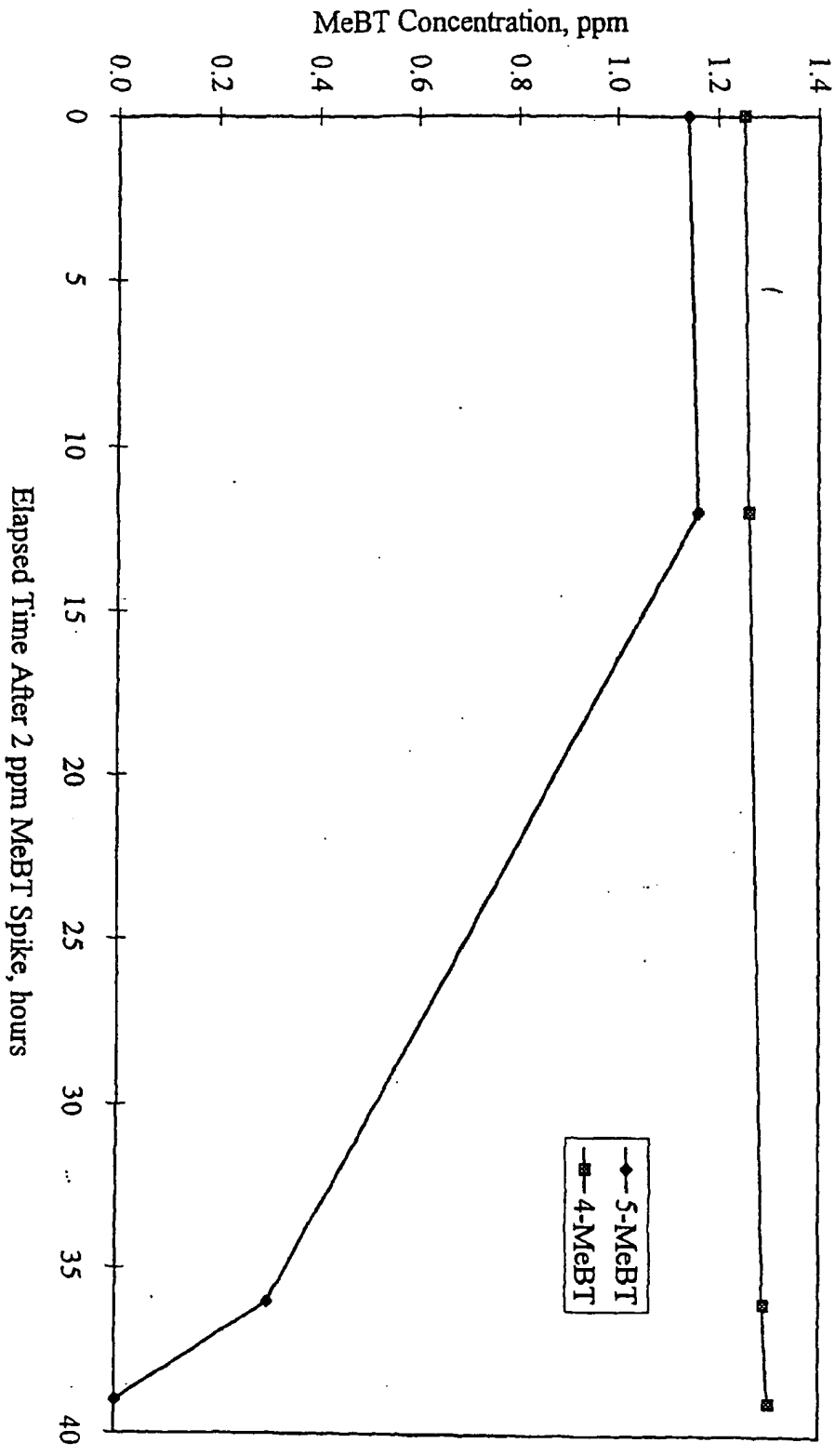

Figure 1. Fate of 5-MeBT and 4-MeBT After TT Spike into Grab Sample of Cooling Tower Water

[drawing(s) replaced or added]

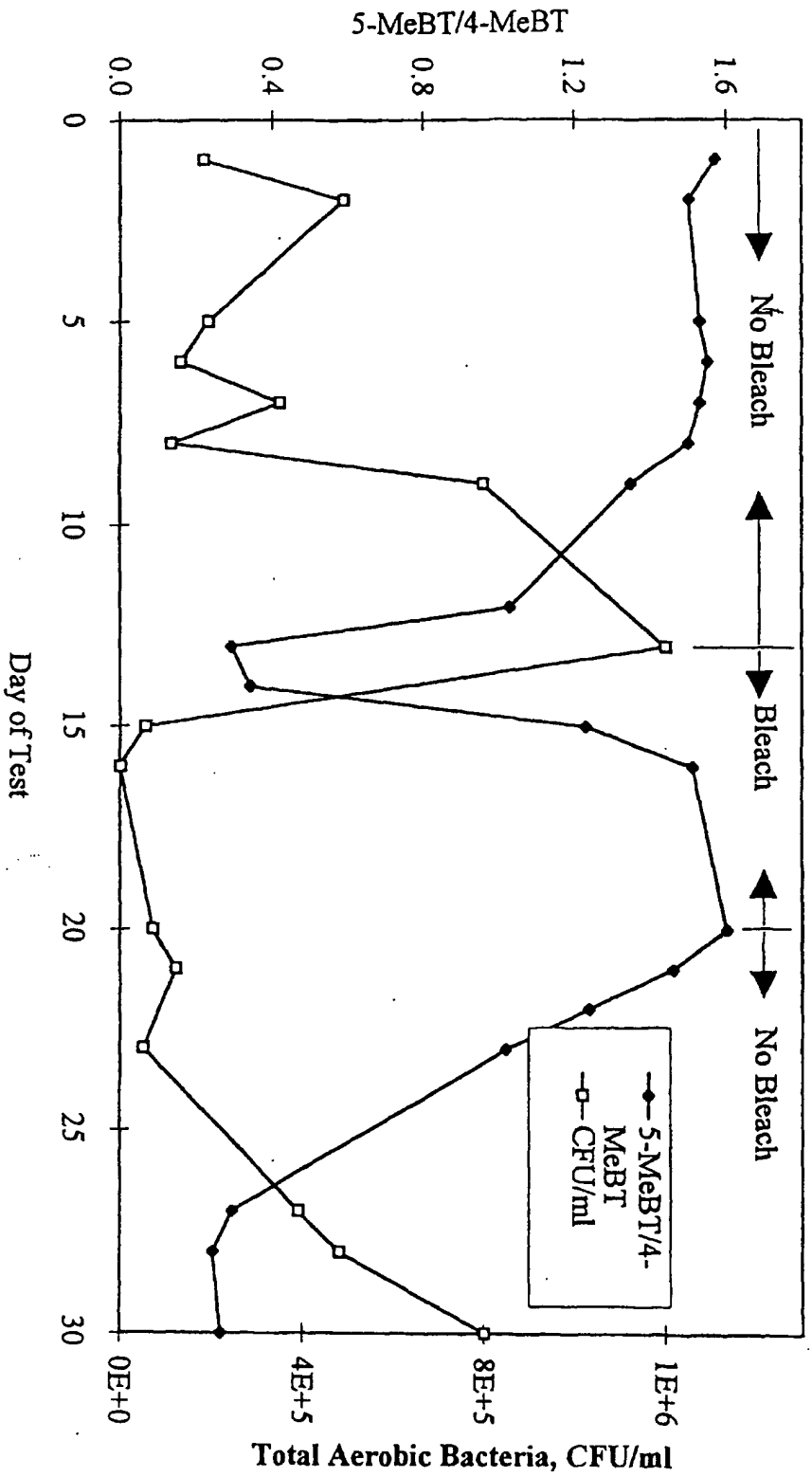

Figure 2. Pilot Cooling Tower Test Showing Effect of Microbiological Population on MeBT Levels

[drawing(s) replaced or added]

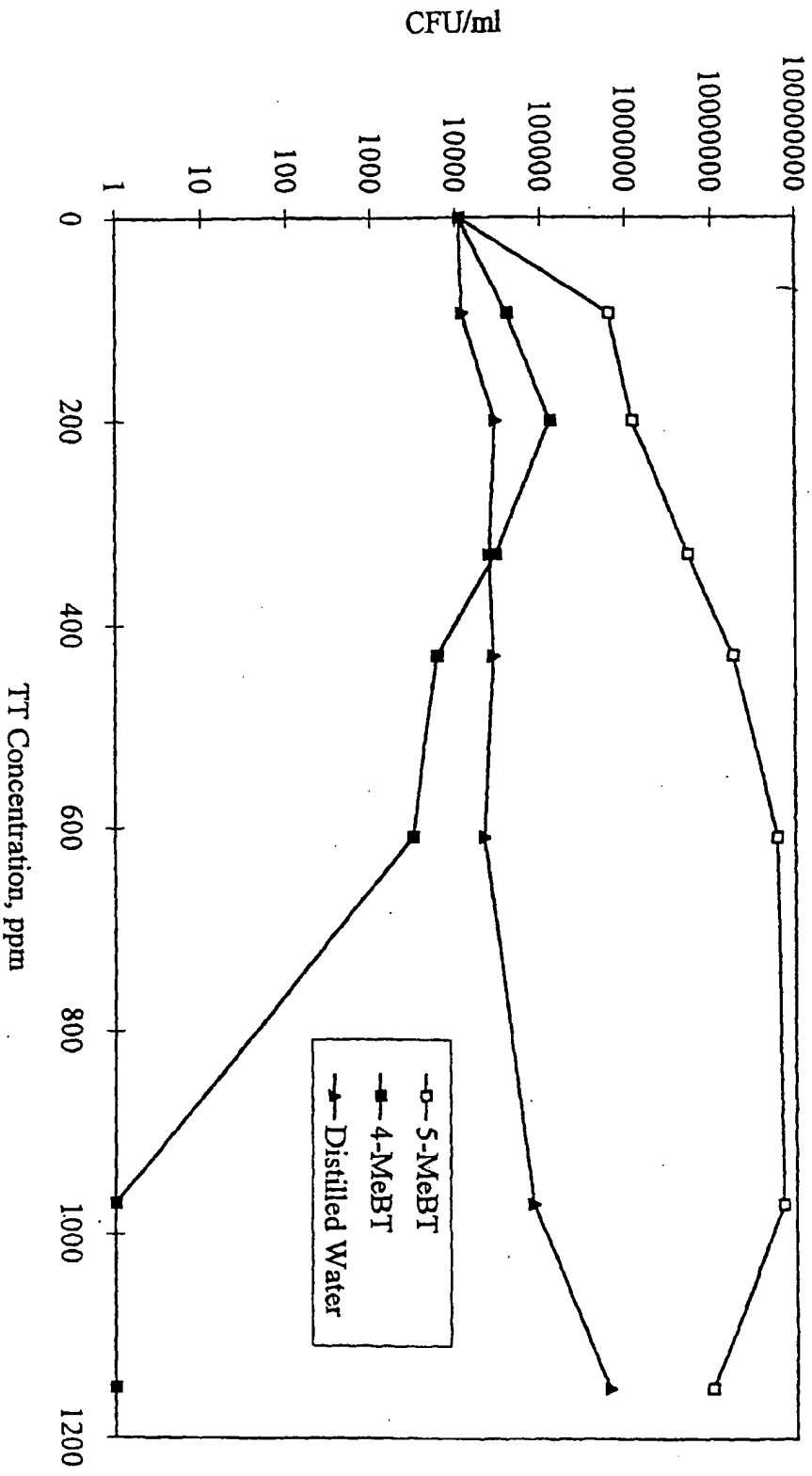

Figure 3. Bacterial Populations as a Function of Dosage of 5-MeBT, 4-MeBT and Distilled Water

[drawing(s) replaced or added]

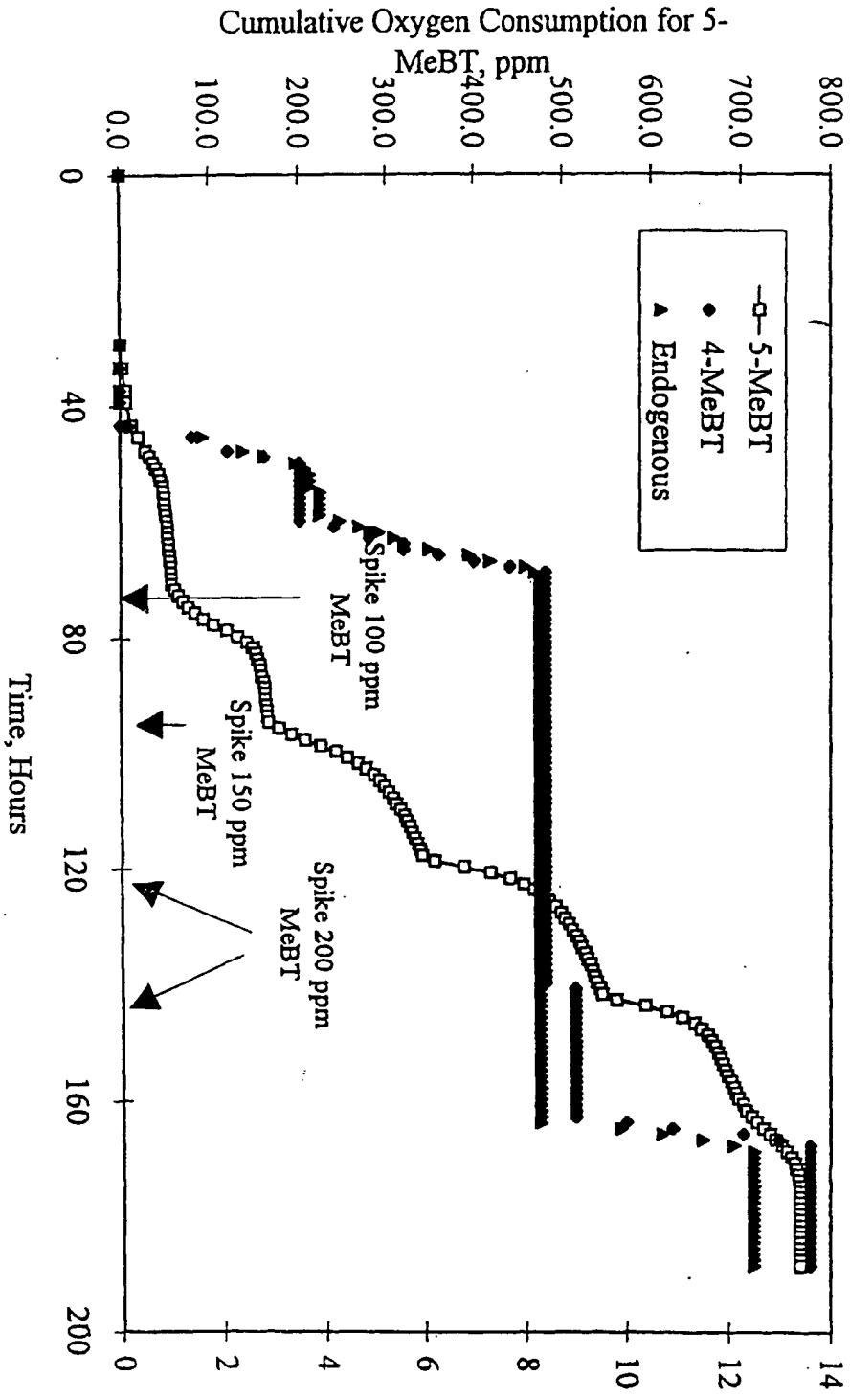

Figure 4. Results of Respirometry Experiment Demonstrating the Aerobic Biodegradation of 5-MeBT